Autobiography of Klaus Ruedenberg

Downloaded via 49.36.181.161 on January 23, 2024 at 23:07:40 (UTC).
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

Growing Up

Born in 1920, I grew up in Bielefeld, then a city of about 100,000 in Westphalia, Germany. For about a century, my parents' families had developed successful and respected textile manufacturing and retail businesses in the county, which had been part of Prussia since the end of the Thirty Years' War. As the only child, I received much genuine love from my parents, Otto Ruedenberg and Meta née Wertheimer, including the precept that life is about living up to challenges, ethical, professional, and educational. From 1925 to 1929, I attended the public Diesterweg elementary school. From 1929 to 1938, I received a thorough classical-humanistic education at the public Gymnasium: An hour of Latin every day for eight years, an hour of Greek every other day for five years, history, other liberal arts subjects, participatory physical education (gymnastics, soccer, boxing), all of which I liked, but no differential calculus and minimal science.

Coming from a Jewish family, whose businesses were being destroyed by the government, I was keenly aware of and much affected by the discriminations that developed increasingly strongly in everyday life after Hitler had come to power in 1933. Nonetheless, the enlightenment tradition still cast its long shadow over the climate at the six centuries old Gymnasium, and I did not suffer persecution or indignities from teachers or fellow students. We still read Lessing's *Nathan the Wise*. The only exception was the opportunistic principal, newly appointed in the mid-thirties, who on one occasion humiliated me in front of our class of about 15 students by an abusive dressing down over an action that he construed as Jewish irreverence on my part. Remarkably and unbeknownst to me, a group of four classmates then went jointly to the principal protesting the unfairness of his allegations. There was of course a general tightening climate of fear that kept me isolated in many ways. For instance, the apologetic student head of the gymnastic club informed me that the authorities forced the club to expel me, and, much later, I was told that the teachers had been afraid to give me A's instead of B's. A classmate (Alfred G. Meyer, later a professor in political science at the University of Michigan) and I were in fact the last Jewish students permitted to graduate with the *Abitur* from that Gymnasium.

I was though very fortunate to enjoy a close friendship with a classmate, Victor Georg Köhler. For years, we sat next to each other during class and on most days spent time after school together. His father, a colonel in the army and of a towering stature, despised the Hitler regime and told his son that a man of Prussian honor stands by his friends no matter who they are. Like all my classmates, my friend was subsequently drafted into the army and contracted permanent damage to his health as a prisoner in Russia. After the war, my wife's family invited him to spend a year for studies in Switzerland.

Switzerland

My parents had made contact with the Institut Montana in Zugerberg which, after looking me over, offered me a fellowship. Thus, I left home in the spring of 1938 and spent a little over a year at this international Swiss preparatory school in the English section, where I learned English history, English literature, the beginnings of differential calculus, and played much soccer. In the summer of 1938, my parents visited me there and, ignoring a Swiss friend's warning, returned home. In November, the Kristallnacht happened. I left the school in the fall of 1939 during the first days of World War II and, not being granted a Swiss permit to work, I was supported by charitable institutions and friends of my parents for the next nine years. For a relatively small fee, I could attend universities however.

Following my parents wishes, I enrolled in Chemistry at the University of Fribourg, where a relative of my mother was married to the Swiss Law Professor Max Gutzwiller. His family was indeed very gracious toward me and I still am a personal friend of one of the sons, Martin Gutzwiller, who became an internationally renowned physicist. The first three years of my studies involved heavy, merciless qualitative as well as quantitative analytical laboratory work, whose rigor conveyed to me what true science is about. Although I spilled boiling sulfuric acid over my hand and blew up an Erlenmeyer flask in which I generated hydrogen gas in front of me, I rather liked the laboratory. My professors were Henri de Diesbach and Louis Chardonnens in chemistry, Friedrich Dessauer in physics, and Albert Pfluger in mathematics. During most summer vacations of the war years, refugee students from various Swiss universities had to spend between one and two months in government work camps, inasmuch as all Swiss students were drafted into the mobilized army as border guards during that time. These forced gatherings actually generated many friendships between interesting people in the barracks. Thus, Edgar Heilbronner, then a student with Leopold Ruzicka at the ETH in Zürich and later Director of the Physical Chemistry Institute at the University of Basel, and I became lifelong friends and continued to reminisce how we became experts at felling timber in the Rhone valley. In the summer of 1942, several of us paid a visit to the grave of the poet Rainer Maria Rilke in Raron, not far from one of the camps. At that time, I received word that my mother had died and that, shortly thereafter, my father had been deported to Poland and Russia, never to return.

While I was not an unskilled chemical experimenter, I discovered that my natural inclination and strength really lay in the mathematical approach to the sciences. Upon recommendation by professor Pfluger, who was about to move to the ETH, I was accepted as a Ph.D. candidate in theoretical physics by professor Gregor Wentzel at the University of Zürich, one of the early pioneers in quantum theory. I completed my studies in Fribourg with the *license ès sciences* in 1944 and, about three quarters of a year before the end of the war in Europe, I moved to Zürich. At about the same time, I got engaged to Veronika Kutter, with whom I had become acquainted since her aunt and my mother had been friends for about half a century. Later, I wondered how, as a penniless and stateless young refugee (the Hitler government had divested me of my German nationality), I had the courage to ask for the hand of the exceptional daughter of an established Swiss family. But my mentor, the above-mentioned Max Gutzwiller, wisely remarked that, common perceptions to the contrary, most good relationships have their origins in the woman having made the initial choice and decision.

10.1021/jp1056013 © 2010 American Chemical Society
Published on Web 08/19/2010

In Zürich, Wentzel's outstandingly lucid lectures proved to be an eye-opening introduction into the entirely new world of theoretical physics, which also meant, however, that, to some degree, I had to start over my studies. Every week there was a seminar in theoretical physics, chaired by Gregor Wentzel and by Wolfgang Pauli of the ETH, sometimes also attended by Ernst Stückelberg from Geneva and Markus Fierz from Basel, in which students often had to report on the recent literature. It was an intimidating experience. My mathematics professors were Rudolf Fueter, Paul Finsler, Michel Plancherel, and Heinz Hopf. The latter's beautiful and insightful lectures on advanced linear algebra turned out to be invaluable for my later work in quantum chemistry, and Fueter's lectures on differential geometry provided a good basis for my understanding of potential energy surfaces. Being a theoretical physicist, I had to give only one of the mathematical seminars. I remember visiting lectures by Erwin Schrödinger, Werner Heisenberg, and Constantin Carathéodory. After three years, I began with my thesis in quantum field theory on the strong coupling between nucleons and pseudovector mesons and the resulting internucleon forces. It was then standard in theoretical physics to meet with the thesis advisor about once a month to discuss the progress made.

A year later, Gregor Wentzel accepted a professorship at the University of Chicago, and its physics department offered me a graduate assistantship so that I could complete the work with my advisor. With this prospect, Veronika and I decided to marry and, without any expression of misgivings, her family prepared a beautiful wedding for the daughter who was soon to leave them for the new world and was in fact also becoming stateless by this marriage. In September 1948, we traveled through devastated Europe to Rotterdam and crossed the cold and choppy North Atlantic in one of the smaller Dutch steamships. After a short visit with a relative, Reinhold Rudenberg, head of the Department of Electrical Engineering at Harvard University, the New York Central Railroad took us to Chicago. Our life in the Windy City began in a cheap two-room apartment in Woodlawn at the very moment when this "community area" was on the verge of a decade of radical racial transitions and tensions.

Chicago

Many members of the formidable Physics Department at the University of Chicago had been involved in the Manhattan Project. C. N. Yang and T. D. Lee were the brilliant students of Enrico Fermi, whose lectures consistently and elegantly cut through the formal trappings to bring the physical essence into focus. He proved to be very kind when I had to give a seminar. A remarkable experience was when, halfway through a lecture by Edward Teller on the nuclear shell model, Maria Goeppert-Mayer in a very quiet voice took all the wind out of his full sails by pointing out a rather elementary, but fatal flaw in his assumptions. At that moment, one could have heard a pin drop in the large audience. My thesis was completed in 1950, published in Helvetica Physica Acta and approved by Walter Heitler, the successor to Gregor Wentzel at the University of Zürich, which awarded me the Ph.D. degree in 1951.

In view of my background, I thought that it might prove fruitful to combine my training in chemistry and in quantum theory. Serendipitously, Robert S. Mulliken, then one of the few leaders in this field, was also a member of the physics department and willing to accept me as a postdoctoral fellow. On the other hand, the physical organic chemist George Wheland strongly advised me against this career choice because, as he put it, "you will never be able to calculate anything useful". In view of the then available means for quantitative computations, he was absolutely right, and I would have come to regret my decision to disregard his counsel had it not been for the revolutionary subsequent development of electronic computers.

Before joining Mulliken, I spent three enjoyable months in Pittsburgh at the Carnegie Institute of Technology at the invitation of Robert G. Parr, from whom I received my first introduction to quantum chemistry.

Ab Initio Integrals *versus* Free Electron Model

Robert S. Mulliken had a vast knowledge and a legendary intuition for the successful semiempirical analysis of molecules, and every discussion with him was enormously rewarding. However, he had come to the conclusion that a more rigorous approach, for which he had chosen the name *ab initio*, should be attempted. In charge of this project was Clemens Roothaan, then a postdoctoral associate who had recently completed his thesis with Mulliken.

When I joined the effort, the "bottleneck to be broken" was the calculation of electron repulsion integrals between exponential-type atomic orbitals on two centers, of which the exchange integrals were the hardest. Through an integration by parts, I was able to reduce this six-dimensional integral to a simple one-dimensional numerical quadrature over functions derived from charge-density distributions, an entirely novel approach. The method proved essential for the first full *ab initio* calculation of a molecule beyond H_2, namely the SCF investigation of N_2 with a Slater-type minimal basis by Charles Scherr (on electric desk computers), published in 1955. The new approach proved so effective for the *simultaneous* evaluation of the large numbers of such integrals required in molecules, in particular on electronic computers, that it was also adopted for evaluating other electron repulsion integrals. This workhorse became an essential requisite in all *ab initio* calculations on diatomic and also other linear molecules that were performed with exponential orbitals since then, notably over the next decades in Mulliken's laboratory and at the IBM Research Laboratory in San Jose, California.

On the other hand, interactions with John R. Platt, who had recently elucidated the electronic spectrum of benzene by means of free-electron concepts, led Charles Scherr and me to develop a free-electron *network* model for π-electrons in conjugated hydrocarbons, which we demonstrated to be *isomorphic* with the Hückel-type tight-binding model. By generalizing the model, Norman S. Ham and I were then able to elucidate the spectra of a series of large cata- and peri-condensed aromatic systems.

While the work on integrals had been recognized as important at the *Shelter Island Conference on Quantum Mechanical Methods in Valence Theory* in 1951, which had brought together most researchers (26) in that field, I could not fail to notice that, because of the manifest relation to experiment, the work on π-electron spectra found much wider interest at other meetings. To this day, the free-electron network model has remained an elucidative vehicle for conceptual interpretations of tight-binding approximations.

John Platt also vouched to the federal government for my personal character when, in 1955, I became a citizen of the United States.

Iowa

One of the very few chemistry departments where the physical chemists believed in the coming importance of theoretical chemistry was at Iowa State University in Ames. Frank Spedding, the director of the Ames Laboratory of the U.S.

Atomic Energy Commission, had worked on unscrambling atomic spectra of rare earth atoms, Robert Rundle had found molecular orbital concepts useful in explaining molecular structures established through his acclaimed X-ray analyses (he had predicted three-orbital–four-electron bonded noble-gas halides before they were found), Robert S. Hansen was a widely known experimental and theoretical surface chemist, and Lawrence Bartell was a pioneer in the electron diffraction of molecules. In 1955, they contacted Mulliken and Platt in order to find a replacement for Harrison Shull who had moved from Ames to the University of Indiana. My choice of the free-electron work on electronic spectra for my interview seminar proved wise: I was offered the position. Veronika was happy to be living with our two little children in a small house on four acres in nature rather than within the unsafe confines of big city concrete.

While there had been a consensus at the Shelter Island Conference that there was a need for *printed tables* of molecular integrals, it had become apparent by 1955 that future calculations were going to be performed entirely within electronic computers, which had since become available. I therefore joined the X-ray crystallographers, the statisticians, the econometricians, and the electrical engineers in urging the provost of Iowa State University to finance electronic computation. By 1959 we started using a copy of the ILIAC, a machine based on the von Neumann architecture (1000 words primary memory, secondary storage on paper teletype tape), which the electrical engineers had built at Iowa State University. Within a decade, the university had IBM mainframe computers. In our first calculations, R. L. Hummel and I generated the visible and ultraviolet spectra of 37 unsaturated hydrocarbons, using an overlap-augmented tight-binding approximation that I had developed. Considering the simplicity of this semiempirical model, it approximated the experimental spectra remarkably well.

The years 1962–64 I spent at Johns Hopkins University, after which I returned to Iowa State University.

Origin of Covalent Binding and Electron Localization

Teaching quantum chemistry brought me face to face with the fact that there existed a confusingly great number of partially contradictory rationalizations why electron sharing yields covalent binding and how various postulated bonding interactions fit together. Notably, the solution of a homework problem I gave revealed that Mulliken's famous resonance integral was negative due to its kinetic component and not, as generally assumed, due to its potential component. These observations prompted me to examine the general expression of molecular densities, pair-densities, and energies in terms of constituent atomic orbitals, an effort that resulted in the first exhaustive "energy decomposition analysis" for *ab initio* wave functions. Although it was too exhaustive for thorough general quantitative explorations at the time, the conceptual basis was sound, and it led to a rigorous elucidation of the origin of covalent binding in H_2 and H_2^+. Unexpectedly, this work landed me in the midst of a contentious conceptual controversy that had been brewing for 30 years, namely, whether covalent bond formation was the result of changes in the kinetic or the potential energy functional. My detailed quantitative analysis showed that, ultimately, the kinetic energy changes were the responsible element, and that, contrary to some prior claims, this fact was in perfect harmony with the virial theorem. While R. S. Mulliken, K. Fukui, W. Kutzelnigg, and others soon espoused this reasoning in their books, the part of the theoretical chemistry establishment that had previously prevailed in disseminating the opposite view was not amused and, even today, many textbooks still perpetuate incorrect explanations.

Ever since, the extraction of correct physical and chemical interpretations from accurate and hence necessarily complex electronic structure calculations, especially as regards bonding, has remained a challenge that has attracted my attention. My graduate student Clyde Edmiston initiated work on localized SCF orbitals, and our cooperation led to the general determination of such orbitals by solving the maximization problem of the localization criterion posed ten years earlier by John Pople and J. E. Lennard-Jones. We moreover proposed two new localization criteria, to which our algorithm also applied, one of which was subsequently further developed by S. F. Boys. Important algorithmic simplifications were added by Richard Raffenetti.

The paper on the origin of chemical binding (1962) and that on localized orbitals (1963) became two of the 100 most cited articles published between 1955 and 1988 in the *Reviews of Modern Physics*. They raised numerous questions, which several co-workers and I addressed over the next decade. In addition to Clyde Edmiston, they were Roland Rue, Allen Wasserman, Melvin Feinberg, Ernest Mehler, Lydia Salmon, Walter England, and notably Mark Gordon. Among other issues, this work elaborated the relationship between the origin of binding and the variation principle, identified characteristics of localized orbitals in systems from diatomic to organic molecules, and defined the real meaning of delocalization in conjugated, especially aromatic, π-systems.

The work on these problems also set in motion a rewarding and enjoyable long-term collaboration with Eugen Schwarz on problems of electron densities and chemical binding in molecules and crystals.

Zeroth Order Electron Correlation: MCSCF and ALIS

During the 1960s, Kenneth Miller, Ernest Mehler, David Silver, and I also began to look at the problem of electron correlation by determining the first quantitative *ab initio* separated-pair wave functions including orbital optimization. While the results (viz., for the atomic systems Li^- to Ne^{6+} and for the potential energy curves of LiH, BH, and NH) were extensively discussed in Andrew Hurley's book (1976) on electron correlation, they taught us that chemical applications called for higher levels of correlation. We therefore started to search for an efficient *general* multiconfigurational self-consistent-field (MCSCF) method. Following up on a proposal by Fritz Grein from the University of New Brunswick, Lap Ming Cheung and I developed in the early 1970s one of the first rapidly convergent "super-CI" MCSCF methods based on the combined use of the Brillouin–Levy–Berthier theorem and natural orbitals. We would not have reached this goal, however, without several additional simultaneous developments.

While the diatomic separate-pair calculations had been performed with exponential-type atomic orbitals, for which we had developed new integrals codes (by Kiyosi Oohata, David Silver, Ernest Mehler, and Ralph Christoffersen), explorations of the difficult multicenter integrals between exponential atomic orbitals (with Otto Steinborn and Lydia Salmon) convinced us that work on polyatomic systems would have to be based on contractions of the Gaussian atomic orbitals proposed by Frank Boys, as they were then being developed at various laboratories. When Richard Raffenetti, Richard Bardo, and I took a closer look at Sigeru Huzinaga's and Kiyosi Oohata's Gaussian expansions of atomic SCF orbitals, we discovered that only an inconsequential loss in accuracy was incurred when, instead of the independent optimization of all exponents, the latter were expressed as a geometric series so that only the two parameters of that series had to be optimized. Moreover, these orbital were less prone to become linearly dependent because of their sequential equidistance in function space, which suggested to us the name *even-tempered* orbitals. Later work with David Feller established analytic relations between them and exponential expansions, while Werner Kutzelnigg showed how such sets generate systematic approximations to complete basis sets. Later, Michael Schmidt and I determined even-tempered sequences for SCF orbitals of all atoms up to argon, identified numerous regularities, and thereby could generate closer approximations to the Hartree–Fock limits, from above and below, than were available at the time, numerically or analytically. The advantages of even-tempered orbital sets are such that they have been widely used in many contexts ever since. They have for instance been workhorses in the development of Thom Dunning's famous correlation consistent basis sets. Richard Raffenetti obtained equally accurate nonrelativistic SCF approximations for atoms up to Lanthanum by using much smaller even-tempered *exponential* orbital sets.

Two other components were essential for our MCSCF program: An integral evaluation code for Gaussian primitives and a code for Hamiltonian matrix elements. Richard Raffenetti created the former by implementing Sigeru Huzinaga's formulation. He moreover constructed one of the first efficient methods for calculating integrals between *general* contractions, rather than the then common *segmented* contractions, so that we could use arbitrary contractions of eventempered primitives. The formulation of the Hamiltonian matrix, on the other hand, was contingent on the formulation of the configurational basis. Because of my choice of spin-adapted antisymmetrized products with Serber spin functions, the coupling coefficients for the orbital integrals became the representation matrices of the symmetric group, and William Salmon ably worked out the intricate details. From the mid-1970s on, Stephen Elbert integrated all the parts into an efficient, coherent whole, improved many aspects, created efficient integral transformations between MCSCF iterations, and implemented state-of-the-art diagonalization techniques. The result was the ALIS (for **A**mes **L**aboratory **I**owa **S**tate University) MCSCF program that we used over the next decade and that became also part of the program library of the National Resource for Computational Chemistry at the Lawrence Berkeley Laboratory. While the subsequent developments of the graphical unitary group approach and the determinant-based direct configuration interaction method turned out to be able to handle very much larger *full* configuration spaces, the ALIS program had the unique feature that it could handle configuration spaces spanned by *arbitrary* configuration selections. Because of this capability, it continued to be used by researchers whose interest lay in the exploration of the importance of specific configuration selection schemes in achieving specific objectives.

Around 1980 our group received a copy of Michel Dupuis' program GAMESS and Stephen Elbert began to incorporate certain elements from ALIS into it. Michael Schmidt took copies of both ALIS and GAMESS with him when he joined Mark Gordon a few years later at North Dakota State University. Toward the end of the 1980s Stephen Elbert spent two months helping Joachim Werner in Bielefeld with the MOLPRO program and brought one of its first versions to Ames.

Full Optimized Reaction Space: Chemical Interpretation and Bond Breaking

The MCSCF capability enabled us to examine rigorously an old assumption in quantum chemistry, namely, that molecular wave functions can be conceptually constructed from *minimal basis sets*, a term also coined by Mulliken, and that the molecular orbital and the valence bond approaches would become identical when pushed to their full extent within this minimal basis set framework. In order to see how well this idea played out in rigorous quantum mechanics, Lap Ming Cheung, Kenneth Sundberg, and I, in the early 1970s, started to determine and examine MCSCF wave functions in what we called the *"Full Optimized Reaction Spaces (FORS)"*, i.e., when the valence electrons in a molecule are given the opportunity to make full use of *all* configurations that can be generated from M orbitals, where M is the *total number of conceptual minimal basis set orbitals* in the molecule. We were delighted to find that subsequent localization yielded orbitals that had indeed the character of deformed atomic minimal basis set orbitals. These *quasi-atomic FORS molecular orbitals* represented thus the optimal rigorous realizations of the early intuitive qualitative anticipations, and their occupations and bond orders lent themselves to chemical interpretations. The "full-space" wave function approach, though without restrictions on the orbital number M, was independently developed and published 1980 by Björn Roos, who called it the "Complete Active Space SCF (CASSCF)" method, and it subsequently became widespread under this name.

In addition to providing a rigorous basis for chemical interpretations, FORS wave functions are size-consistent with respect to bond breaking and therefore provide sound zeroth-order approximations for the calculation of energy curves along reaction paths on potential energy surfaces. For such purposes, even suitably *reduced* FORS spaces proved adequate. Work with Lap Ming Cheung, Ken Sundberg, Mary Gilbert-Dombek, and David Feller elucidated such curves for the dissociation of ethylene into two methylenes, the concerted dissociation of dioxetane into two formaldhydes, and the isomerization between HNO and NOH, by using quasiatomic orbitals. Toward the end of the 1970s, a study with Michael Schmidt showed that the concerted dihydrogen exchange between ethylene and ethane, even though formally symmetry-allowed, has a high barrier.

Using the ALIS program, Brenda Lam, Michael Schmidt, and I also created a full-optimized-valence-space adaptation of the *Atoms-in-Molecules Intra-Atomic-Correlation Correction* approach that William Moffit and Andrew Hurley had advanced 30 years earlier and, in this way, obtained estimates for the *dynamic* correlation contributions to the dissociation energies of a series of diatomic molecules.

Global Potential Energy Surfaces

At that point, I became curious about what actual rigorous global potential energy surfaces really looked like. Thus, around 1980 Petros Valtazanos and I began work on the potential energy surface describing the ring-opening of cyclopropylidine $H_2C_3H_2$ to allene $H_2C{=}C{=}CH_2$, a problem of basic interest in organic chemistry. Later, Sotiris Xantheas joined us in this effort. On 32 cross sections (see cover picture), the full energy surface was mapped out as a function of all three reaction coordinates, viz., the ring-opening angle and the two CH_2 rotation angles, with all twelve remaining internal spectator coordinates being optimized at all points of the surface. We found that the reaction path bifurcated after the transition state and that, on the downhill path toward the two stereoisomeric products, the methyl groups could rotate freely, though synchronously. With substituted reactants, the ring-opening was found to be stereospecific. It was a *tour de force* for that time (on a VAX 11/780 computer), but the extensive results have never been challenged, even by some later work with more sophisticated wave functions.

In the second half of the 1980s, Sotiris Xantheas and I started to tackle the reaction surface for what we thought was a simpler ring-opening, namely, that of the ground state of ozone (whose unequivocally predicted ring isomer has yet to be found experimentally). A surprise awaited us, however, near the barrier. Not only did the excited state of like symmetry have its minimum extremely close to the transition state of the ground state but, moreover, the two states met nearby in a conical intersection. Since such a degeneracy contradicted general expectations for two closed-shell dominated states (weak noncrossing rule) and had never been encountered before, we nailed it by quantitatively demonstrating the phase inversion of the MCSCF wave function on a closed loop, the first such verification for a large multiconfigurational wavefunction. We furthermore showed that it was a consequence of strong *correlation changes within the two diabatic components* of the two states. In the early 1990s, Greg Atchity and I determined and discussed the global surface for both states as well as the closed intersection seam.

Greg Atchity, Joseph Ivanic and I subsequently showed the existence of similar conical intersections in the valence iso-electronic molecules S_3, SO_2, and OS_2. An investigation of CO_2 with Sotiris Xantheas showed that its potential energy surface, too, had a metastable ring structure.

Analysis of Potential Energy Surface Features

The work on global potential energy surfaces led us to examine in greater depth certain distinctive surface features. Thus, in connection with the study of cyclopropylidene, Petros Valtazanos and I analyzed algebraic prototypes for the differential geometries around valley-ridge inflection points, which elucidated the surface contour patterns that can occur when a reaction path bifurcates before, at or after a transition state.

Work with Jun-Qiang Sun in the early 1990s yielded an efficient second-order steepest descent integration, which Joachim Werner subsequently also incorporated in the MOLPRO program. We then showed that orthogonal trajectory *maps* exhibit surface characteristics not readily apparent from contour maps and found in particular that *reaction channels* require the existence of steepest descent line bundles that gather around gradient extremals. The latter curves, which David Hoffman and I had previously introduced and discussed, are completely defined by *local* differential criteria, in contrast to steepest descent lines. The work with Jun-Qiang Sun also yielded a transition state approximation that can be derived from the mere knowledge of the reactant Hessian and the product Hessian.

On the other hand, the study of ozone led to clarifications regarding conical intersections. A detailed analysis of the potential energy surface patterns that are possible near intersections, with Sotiris Xantheas and Greg Atchity, became an influential paper. An investigation with Greg Atchity demystified several puzzling aspects of the geometric phase theorem of adiabatic states, notably the *seemingly long-range* effect of intersections, by reducing the phase change to a sequence of *local* interactions between diabatic states. We were also the first to find *intersections of intersection seams* and formulated the more general form of the phase theorem under such circumstances. In this context, Greg Atchity and I also developed a method to determine diabatic states through the "enforcement of configurational uniformity", an approach that provided the basis for subsequent developments by Don Truhlar.

Changes

I was fortunate that Mark Gordon succeeded me as the theoretical chemist in Ames after my obligatory retirement in 1991. Mark's unaltering respect, generosity, and supportiveness have made the continuation of my scientific endeavors a happy experience. The interactions with him as well as with Mike Schmidt have been fruitful, and the close contact with his research group stimulating. Mark's friendship proved particularly meaningful during the years when I took care of Veronika before she died of Alzheimers disease in 2004.

Ab Initio Bonding Patterns

In the middle of the 1990s, Joseph Ivanic joined me from Australia. With the availability of the greatly advanced GAMESS codes, we returned to the problem of *intrinsic identification* of chemical bonding patterns that are *inherent* in *ab initio* wave functions. We developed the first method that extracted *chemically directed quasi-atomic* orbitals from FORS wave functions by an unbiased, basis-set-independent formalism without preconceived bonding information input, and we showed its usefulness in molecules and reactions with a variety of bonding patterns. A method for deducing similar quasi-atomic orbitals from SCF or DFT wave functions was the result of a cooperation with Wencai Lu, Kai Ming Ho, C. Z. Wang, from the Physics Department, as well as Michael Schmidt, and proved extremely useful for work in condensed matter problems. The challenge of these subjects continues to hold my attention. More recently, Eugen Schwarz got me involved in extending the variational analysis of covalent binding to molecules with many electrons and a collaboration with Sotiris Xantheas, Vassiliki-Alexandra Glezakou, and Stephen Elbert exhibited the gradual increase in biradical character from SO_2 to S_3 to O_3 to OS_2.

In the course of this research, Joe Ivanic and I had an unusual experience with a paper in which we provided the first rapid and stable method for determining the rotation matrices between spherical harmonics (by recursion, very different from Wigner's Euler-angle-based formulas). It turned out that our algorithm was just what was needed by computer animation software engineers for the task of generating illuminated 3-D imaging ("spherical harmonic lighting"), and appears now to be used worldwide in that field. Cheol Ho Choi, with whom I developed this method further, regretted that Joe Ivanic and I had not taken out a patent.

Electron Correlation

Joe on the other hand had decided that GAMESS needed a direct determinant-based configuration interaction program and, within a relatively short time, he produced an excellent implementation of the string-based algorithm by Nick Handy and Peter Knowles. At my insistence, he moreover generalized it so that it could be used with *arbitrary* configuration selections and, after having joined the National Cancer Institute, he further generalized it to the *Occupation Restricted Multiple Active Space* method, which became an extremely useful module of the GAMESS suite. These codes enabled us to analyze in detail the actual convergence of configuration interaction expansions and to show that all full configuration spaces contain large amounts of deadwood. Work with Laimutis Bytautas, who joined me around the turn of the century, yielded a method for the *a priori* identification of such configurational dead-wood.

We also invalidated the widely held dogma that natural orbitals generate the most rapidly convergent configuration interaction expansions by demonstrating that "split-localized" orbitals were superior in this respect.

The main achievement of my work with Laimutis Bytautas was the development of the *Correlation Energy Extrapolation by Intrinsic Scaling (CEEIS)*, which, in combination with established complete-basis-set extrapolations, has led to the first systematic approximation to the full correlation energy with subchemical accuracy along reaction paths where multireference zeroth-order correlations are essential for bond breaking. This approach yielded the first accurate *ab initio* potential energy curves for F_2 and O_2 that have recovered the vibration−rotation spectra with error bars of about 5−10 cm^{-1}. In F_2 we moreover discovered the first case of a competition between long-range quadrupolar repulsion and dispersion attraction and predicted a resulting small barrier that has caught the interest of ultracold-temperature dynamicists. The method furthermore allowed us to elucidate the range of electron correlation between localized orbitals in a polyatomic molecule, a problem for which we had earlier developed a simple semiempirical estimate.

Hindsight

As I grow older and more critical, I become more and more aware of how much I owe to so many people who have chosen to exert a positive influence in human affairs. Starting with my parents and the friends of my youth under difficult circumstances and those who helped me after my flight to Switzerland. Then there was Veronika, fiercely independent and fiercely loyal. I sensed our commitment when, after fifty years, she concluded "You are the challenge of my life" and I could but echo her sentiment. She, her family, and our four children have filled my life with love.

Professionally, I am indebted to Albert Pfluger, Gregor Wentzel, Robert Mulliken, John Platt and Robert Parr for encouraging my career. In Iowa, several colleagues resolved to foster this first European implant, notably Gordon Danielson in Physics, Harry Svec in Chemistry, as well as Robert Hansen and Tom Barton, directors of the Ames Laboratory, which offered me the opportunity to make contributions to science that I was able to create. The Chemistry Chairman Robert Angelici entrusted me with chairing the committee overseeing the proper progress of our 200 graduate students. There were of course many others including friends on various parts of the globe. My collaborators, students, as well as senior co-workers deserve my greatest appreciation for cheerfully cooperating with me, contributing their ideas as well as their hard work, and putting up with my whims.

I am also grateful for many invitations for extended visits at various institutions: to Max Wolfsberg at Brookhaven National Laboratory, to Per Olov Löwdin at Uppsala and at Sanibel Island, to Giuseppe Del Re at the University of Naples, to Oktay Sinanoglu at Robert College in Instanbul, to Joe Hirschfelder at the University of Wisconsin, to Edgar Heilbronner at the ETH in Zürich, to Melvin Feinberg at Tufts University in Boston, to Ronald Poshusta at Washington State University in Pullman, to George Hammond at the University of California at Santa Cruz, to Sigrid Peyerimhoff at the Friedrich-Wilhelms-Universität in Bonn, to Andrew Hurley at the CSIRO David Rivett Laboratory in Clayton, Australia, to Wilfried Meyer at the Technische Universität Kaiserslautern, to Milan Randic and Ante Graovac at the Inter-University Center in Dubrovnik, to Ramón Carbó-Dorca at the University of Girona, and to Piotr Piecuch and J. Schnack at the European Centre for Theoretical Studies in Trento. Happily, such stays also proved sources of enjoyment for Veronika. At several Sanibel Symposia, her puppet shows brought tears to the eyes of Per Olov Löwdin. Last but not least, I warmly thank those colleagues who made the efforts to steer honors my way, and this also includes those who have organized the present journal issue.

References

The following sequence of subjects corresponds to the sequence in which they occur in the preceding narrative. The numbers refer to the entries in the publication list.

Integrals between exponential-type atomic orbitals
Two center exchange: 3, 26, 54
Other two-center: 7, 39, 40, 44, 48, 49, 50
Multicenter: 4, 80, 83
Expansions of $(1/r_{12})$: 3, 43, 51, 56, 79

Conjugated π-electron systems
Free-electron model: 2, 5, 6, 8, 9, 10, 11, 12, 32, 35
Tight binding LCAO model: 15, 16, 17, 18, 19, 20, 23, 24

Electron sharing and covalent binding
21, 28, 29, 30, 61, 68, 73, 107, 192, 193, 203, 206

Localized orbitals
25, 27, 36, 37, 41, 71, 72, 93, 100, 106, 109, 151

Electron densities
130, 137, 139, 140, 141, 142, 168, 176

Multiconfiguration SCF
Separated pairs: 38, 45, 46, 47, 62, 63, 64
General MCSCF: 115, 119, 136, 180
Symmetric-group-based configuration interaction: 74, 82, 84, 85, 86

Eventempered atomic orbital sets
70, 87, 94, 96, 97, 98, 99, 101, 102, 117, 118

Full optimized reaction space (FORS)
Chemical interpretations: 121, 122, 123,
Chemical Reactions: 108, 113, 114, 124, 127, 128

Global potential energy surfaces
$H_2C_3H_2$: 135, 145, 146, 147, 148
O_3: 144, 149, 153, 165, 166, 167, 170
CO_2: 143, 159

Differential geometry of potential energy surfaces
Bifurcations: 134
Steepest descent: 155, 156, 157, 161,
Gradient extremals: 133, 152, 160
Transition states: 162, 163,
Conical intersections: 144, 150, 153, 172
Diabatic states: 154, 169

Ab initio bonding patterns
182, 183, 184, 189, 199, 200, 209

Rotation and translation of orbitals
65, 81, 91, 164, 173, 174

Electron Correlation
Deadwood in CI: 177, 178, 201
CEEIS: 185, 186, 187, 188, 190,
F_2: 195, 196, 197, 202
O_2: 204, 205,
Ne_2: 198
Be_2: 208
Convergence: 55, 179, 181, 207

Klaus Ruedenberg

JP1056013